Studies on Mechanical Characterization and Water Resistance of Glass Fiber/Thermoplastic Polymer Bionanocomposites

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Received 8 February 2011; accepted 26 April 2011
DOI 10.1002/app.34801

ABSTRACT: This experimental work is aimed at studying the performance of rice husk flour/glass fiber reinforced high density polyethylene hybrid nanocomposites. To meet this objective, the nanoclay was compounded with high density polyethylene (HDPE), rice husk flour (RF), glass fiber, and coupling agent in an internal mixer; then, the samples were fabricated by injection molding. The concentration was varied from 0 to 6 per hundred compounds for nanoclay and from 0 to 15% for glass fiber, individually. The amount of coupling agent was fixed at 2% for all formulations. The morphology, water absorption, thickness swelling, and mechanical properties of nanocomposites were evaluated as a function of nanoclay and glass fiber contents. The results indicated that both modulus and strength were improved when glass fibers were added to the composites system but impact strength and moisture absorption further decreased with the increase of glass fiber content. The morphology of the nanocomposites has been examined by using X-ray diffraction. The morphological findings revealed that the nanocomposites formed were intercalated. The mechanical analysis showed that the biggest improvement of the tensile and flexural modulus and strengths can be achieved for the nanoclay loading at 4 per hundred compounds. However, further increasing of the loading of nanoclay resulted in a decrease of impact strength. Finally, it was found that addition of nanoclay reduced the water absorption and thickness swelling of the composites. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2391–2396, 2012

Key words: thermoplastic polymer; glass fiber; properties; morphology; biocomposites

INTRODUCTION

During the last few decades, thermoplastics have gained ever-increasing acceptance as an important family of engineering materials and are steadily replacing metals in a wide variety of applications. The commercial consumption of thermoplastics has steadily increased, and this trend is expected to continue despite an increase in their prices. This situation has created an impetus for cost reduction via composites by employing fillers in thermoplastics.[1]

In the recent years, natural organic reinforcements such as cellulosic fibers have penetrated slowly into this market because they offer many advantages over most common inorganic fillers. Cellulosic fibers are abundantly available and have lower costs and density. They lead to a reduced wear of processing equipment and are renewable, recyclable, nonhazardous, and biodegradable. The replacement of inorganic fillers with comparable cellulosic fibers provides weight savings and decreases the cost without reducing the rigidity of the composites.[2] Wood fiber/plastic composites (WPCs) can be a cost-effective alternative to many plastic composites or metals in terms of bending, stiffness or weight.[3] Wood–plastic composites are becoming increasingly acceptable to consumers as a replacement for natural wood due to advantages such as durability, permanent color, and reduced maintenance, in spite of their high price.[2,3]

Recently, to improve the physical and mechanical properties of composites, some approaches such as foaming and chemical treatments,[4] and hybridization with other fillers,[5,6] have been considered by researchers.

Hybrid composites are materials made by combining two or more different types of fibers in a polymer matrix. Although in principle several fibers can be incorporated in to the hybrid system, a combination of only two types of fiber would be the most beneficial. By hybridization, it is possible to achieve a balance between performance properties and cost of the composites, which would not be obtained with a single kind of reinforcement.[5,6] In other words, by careful selection of reinforcements and the processing techniques, it is possible to engineer the material to better suit the various practical requirements with economic benefits.

Glass-fiber-reinforced polymers have been widely used in the automotive and aerospace industries for

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Journal of Applied Polymer Science, Vol. 123, 2391–2396 (2012)

their high strength and low weight properties. The reinforcement of hard ceramic particles in composites improves the performance properties of composite materials.[7] Composites have wide applications in aerospace structures due to their lightweight and high strength. High-damping composite materials that are useful in aerospace structure have to exhibit simultaneously good mechanical properties and high damping capacity. Researchers have reported that incorporation of glass fibers with natural fibers such as wood fibers, sisal, oil palm fibers, pineapple leaf fibers, and bamboo fibers in a plastic matrix resulted in improved performance.[8,9]

Nanocomposite technology with layered silicate clays as in situ reinforcement has been intensively investigated. Essential improvements of physical and mechanical properties, thermal stability, flame resistance, and barrier resistance have been observed for various thermoplastic and thermoset nanocomposites at low silicate content.[10–12] Using nanoclay filler in WPC composite has been reported in the literatures.[13–20] Many efforts have been made in the formation of wood–polymer composite to improve such properties so as to meet specific end-use requirements. The aim of this study was to investigate the effect of nanoclay on the mechanical properties and water resistance of rice husk flour/glass–fiber reinforced high-density polyethylene hybrid composites.

EXPERIMENTAL

Materials

The polymer matrix used in this study was high density polyethylene (HDPE) with a melt flow index of 11 g/10 min, and a density of 0.954 g/cm^3 (supplied by Arak Petrochemical Industries, Iran). Rice husk flour (RF) is used as the reinforcing fiber material was from Cellulose Aria (Iran); the average particle size of rice husk flour was 100 meshes. Maleic Anhydride (MA) provided by Merck (Whitehouse Station, NJ) was used as coupling agent. Montmorillonite modified with a quaternary ammonium salt (trimethyl ammonium chloride) of bis-2-hydroxyethyl tallow as an organic modifier, having a cationic exchange capacity (CEC) of 90 mequiv/100 g clay, a density of 1.98 g/cc, and a *d*-spacing of d_{001}=18.5 nm was obtained from Southern Clay Products USA, with the trade name Cloisite 30B. The E-glass fibers used in this study were supplied by Diba Glass Fiber (Iran). A silane coupling agent, 3-methacryloxypropyl trimethoxysilane, was coated on the glass fiber surface. Average glass fiber original lengths were 3 mm length.

Method

Composite Preparation

Before preparation of samples, rice husk flour was dried in an oven at (65 ± 2)°C for 24 h. Nanocomposite profiles consisting of HDPE, RF, glass fiber, nanoclay and coupling agent were weighed and bagged according to formulations given in Table I. The mixing was carried out by a Hake internal mixer (HBI System 90, USA). First the high density polyethylene was fed to mixing chamber, after melting of HDPE, coupling agent, and nanoclay was added. At the fifth minute, the rice husk flour and glass fiber fed and the total mixing time was 13 min. The compounded materials were then ground using a pilot scale grinder (WIESER, WGLS 200/200 Model). The resulted granules were dried at 105°C for 4 h. Test specimens were prepared by injection molding (Eman machine, Iran). Finally, specimens were conditioned at a temperature of 23°C and relative humidity of 50% for at least 40 h according to ASTM D618-99 prior to testing.

TABLE I
Composition of the Studied Formulations

High-density polyethylene (wt. %)	Rice husk flour (wt. %)	Glass fiber (wt. %)	Nanoclay (phc)	Coupling agent (phc)
50	50	0	0	2
50	45	5	2	2
50	40	10	4	2
50	35	15	6	2

Phc, per hundred compounds.

Measurements

The flexural and tensile tests were measured according to ASTM D790-03 and D638-03, respectively, using an Instron machine (Model 1186, England); the tests were performed at crosshead speeds of 2 mm/min. A Zwick impact tester (Model 5102, Germany) was used for the Izod impact test. All the samples were notched on the center of one longitudinal side according to ASTM D256. For each treatment level, five replicate samples were tested.

Water absorption tests were carried out according to ASTM D-7031-04 specification. Five specimens of each formulation were selected and dried in an oven for 24 h at 102 ± 3°C. The weight and thickness of dried specimens were measured to a precision of 0.001 g and 0.001 mm, respectively. The specimens were then placed in distilled water and kept at room temperature. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. Weight and thicknesses of the specimens were measured after 30 days. The values of the water absorption in percentage were calculated using the following equation:

$$\mathrm{WA}(t) = \frac{W(t) - W_0}{W_0} \times 100 \tag{1}$$

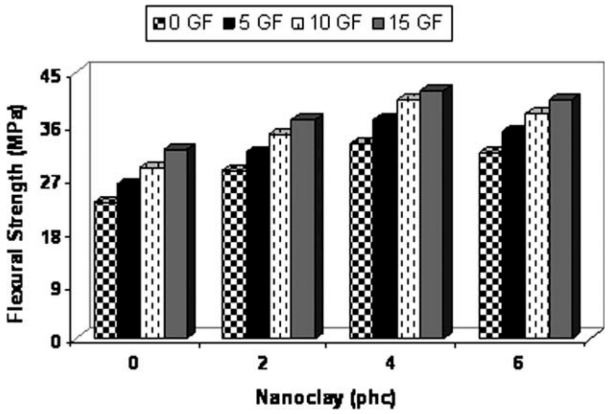

Figure 1 Influence of nanoclay and glass fiber content on flexural strength of HDPE/RF composites.

where WA (t) is the water absorption at time t, W_o is the oven dried weight, and W (t) is the weight of specimen at a given immersion time t.

The values of the thickness swelling in percentage were calculated using the Eq. (2).

$$\mathrm{TS}(t) = \frac{T(t) - T_0}{T_0} \times 100 \qquad (2)$$

where TS (t) is the thickness swelling at time t, T_0 is the initial thickness of specimens, and T (t) is the thickness at time t.

Wide angle X-ray diffraction (XRD) analysis was carried out with a Seifert-3003 PTS (Germany) with CuKα radiation ($\lambda = 1.54$ nm, 50 kV, 50 mA) at room temperature. The scanning rate was 1°/min.

The statistical analysis was conducted using SPSS programming (Version 16) method in conjunction with the analysis of variance (ANOVA) techniques. Duncan multiply range test (DMRT) was used to test the statistical significance at $\alpha = 0.05$ level.

RESULTS AND DISCUSSION

The results of an ANOVA indicated that the nanoclay and glass fiber content had significant effects ($P < 0.05$) on the mechanical and physical properties of composites. The influence of nanoclay and glass fiber content on the flexural and tensile modulus of HDPE/RF composites was shown in Figures 1 and 2, respectively. As can be seen, the flexural and tensile modulus of HDPE/RF composites was affected by glass fiber and nanoclay content. The modulus of composites increased with increase of glass fiber at different levels of nanoclay. It is well established that comparatively different improvements in the HDPE/RF composites may be attributed to the processing technique and the glass fiber form used. This indicates that the effect of hybridization cannot be exploited completely unless the breakage of glass fiber is minimized by modification in the processing techniques. An increase in the strength of HDPE/RF composite as a result of hybridization is expected, as the glass fiber is stronger and stiffer than natural fiber, as reported by other researchers.[6–9,21]

Figures 1 and 2 show that the flexural and tensile modulus increased with increase of nanoclay up to 4 phc at the same concentration of glass fiber and then decreased. It is well known that the nanoclay particles with very high aspect ratio can improve the modulus of the thermoplastic polymer.[16–20,22–24] The increment of the modulus depends on the morphology of nanocomposites.[24–26] The reinforcing efficiency of the nanofiller is balanced by two opposite phenomena. A negative effect is attributed to migration of nanoparticles into the wood–plastic interface, causing decreased performance. At 6 phc of nanoclay, agglomeration of nanoparticles could decrease the reinforcement of clay. Dispersion of nanoclay, as a positive effect, could enhance the modulus; therefore it can be concluded that at a level of 4 phc of nanoclay in the hybrid composite, the former phenomenon was dominant and the tensile modulus increased. It seems that the fully exfoliated morphology can be obtained using higher content of maleic anhydride (MA). In our research in the absence of coupling agent it was not possible to achieve an exfoliated morphology. It is well known that the highest tensile modulus is attributed to an exfoliated morphology in polymeric nanocomposites.[25–27]

The hybrid effect of glass fiber and nanoclay on the flexural and tensile strength of HDPE/RF composite is shown in Figures 3 and 4, respectively. The variation in strength of the composite is similar to tensile modulus. A maximum strength was observed at 15% glass fiber and 4 phc of nanoclay content.

Figure 5 shows the variation of the impact strength versus glass fiber content at different levels of nanoclay in HDPE/RF composites. As can be seen, the impact strength was affected by glass fiber

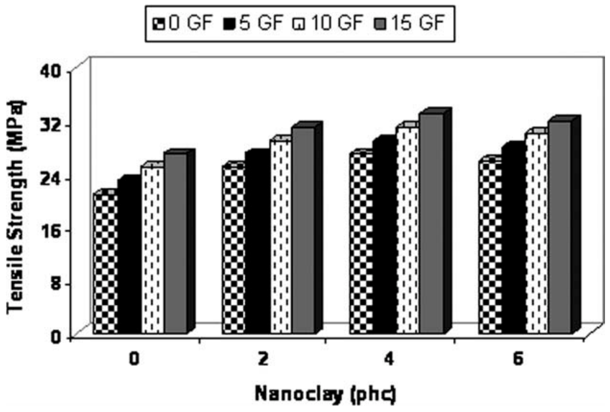

Figure 2 Influence of nanoclay and glass fiber content on tensile strength of HDPE/RF composites.

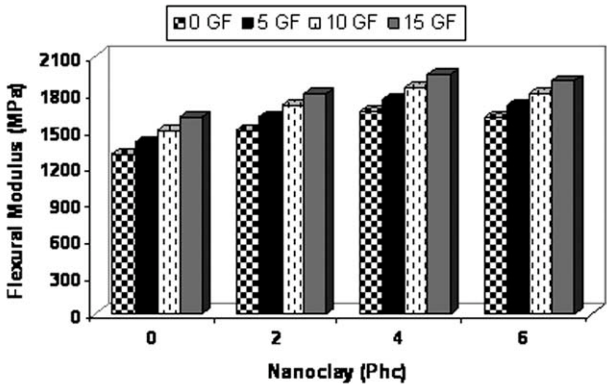

Figure 3 Influence of nanoclay and glass fiber content on flexural modulus of HDPE/RF composites.

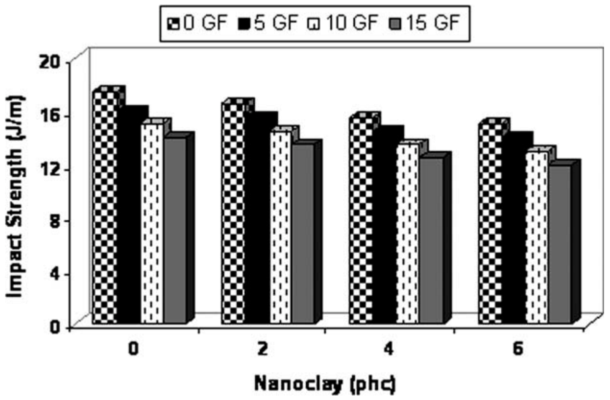

Figure 5 Influence of nanoclay and glass fiber content on impact strength of HDPE/RF composites.

and nanoclay content. The impact strength of nanocomposites decreased with increase of glass fiber at different levels of nanoclay. This could have been due to the effect of brittle glass fiber, which resulted in a lower strength. This shows that the glass fiber content significantly affected the impact properties.[21] Figure 5 shows that the impact strength decreased with increase of nanoclay loading at the same concentration of glass fiber. The decrease in impact strength at higher clay content levels is probably due to the formation of clay agglomerates and the presence of unexfoliated aggregates and voids.[13,28]

The influence of nanoclay and glass fiber content on the water absorption and thickness swelling of HDPE/RF composite is shown in Figures 6 and 7, respectively. As can be seen, the water absorption was affected by glass fiber and nanoclay content. The water absorption of nanocomposites decreased with increase of glass fiber at different levels of nanoclay. Incorporation of glass fiber in the HDPE/RF composites decreased the water absorption significantly, which is attributed to the removal of hydrophilic natural fiber with the glass fiber in the composite. With the increase in the glass fiber content, there are less water residence sites and therefore less water is absorbed. On the other hand, the composites made from higher glass fiber content have less water absorption sites and thus lower water absorption.[21]

Also as shown in Figures 6 and 7, the water absorption and thickness swelling decreased with increase of nanoclay loading at the same concentration of glass fiber. It seems that the barrier properties of nanoclay fillers inhibit the water permeation in the polymer matrix. Two mechanisms have been reported in order to account for this phenomenon. The first is based on the hydrophilic nature of the clay surface that tends to immobilize some of the moisture.[29] The second involves the ability of surfactant-covered clay platelets form a tortuous path for water transport.[30] This barrier property hinders water from going into the inner part of the nanocomposite. It seems both of aforesaid mechanisms could be more efficient when the morphology is exfoliated. In other words in exfoliated morphology, there is more available surface of organoclay (with hydrophilic nature) and surfactant (tortuous path), so the water transport goes down under the severe conditions. Another reason for less water absorption

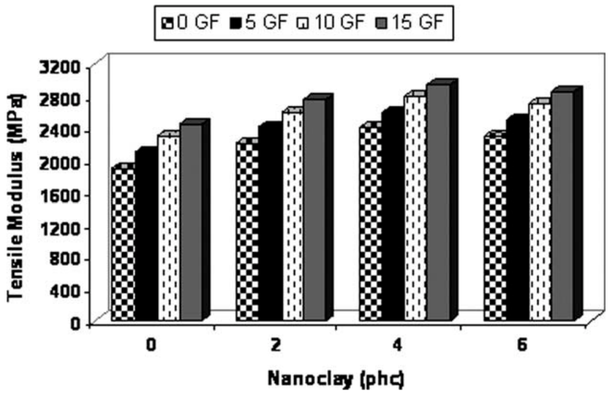

Figure 4 Influence of nanoclay and glass fiber content on tensile modulus of HDPE/RF composites.

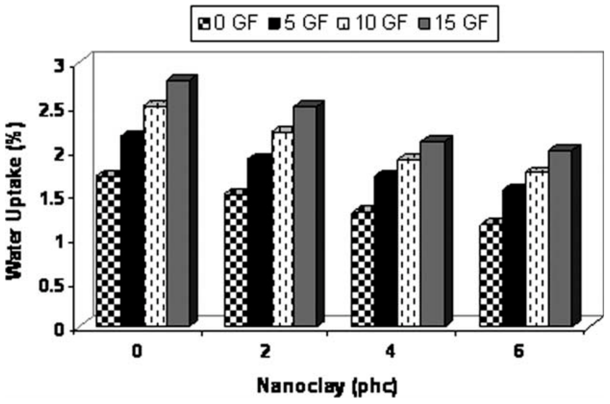

Figure 6 Influence of nanoclay and glass fiber content on water absorption of HDPE/RF composites.

could be the change in crystallinity of WPCs by existence of nanoclay as a nucleating agent.[14–17]

Characterization of the morphological state of the composites was accomplished using X-ray diffraction. To verify a homogeneous dispersion of nanoparticles (so-called intercalation and exfoliation) in a polymer matrix, the interlayer spacing in nanolayered silicates (Bragg's law) and the relative intercalation (RI) of the polymer in nanoclay were quantified using the following equations,

$$n\lambda = 2d\sin\theta \tag{3}$$

$$\mathrm{RI} = [(d - d_o) \div d_o] \times 100 \tag{4}$$

where n is the integer number of wavelength ($n = 1$), λ is the wavelength of the X-rays, d is the interlayer or d-spacing of the clay in the nanocomposite, θ is half of the angle of diffraction, and d_o is the spacing of the clay layers in the pristine clay.

The d-spacing and relative intercalation of the clay in the nanocomposites calculated from eqs. (3) and (4) is listed in Table II. This table shows that the order intercalation of samples increased with increase of nanoclay content up to 4 phc and then decreased. The peaks appearing at 4.76 Å correspond to powdered nanoclay with $d_{001} = 18.5$ nm. In the sample with the addition of 2 phc nanoclay, the peak was shifted to a lower angle ($2\theta = 3.70$ Å, $d_{001} = 23.83$ nm), which implies formation of the intercalation morphology. The increase of the interlayer distance and relative intercalation might result from the stronger shear during processing when rice husk flour was introduced. These data show that the order of intercalation was higher for 4 phc of nanocaly ($2\theta = 3.09$ Å, $d_{001} = 28.47$ nm). Also, the clay was not exfoliated, since the peak still obviously existed. In other words, formation of the intercalation morphology and better dispersion was shown in 4 phc of nanoclay, because the peak of that was shifted to a lower angle. It seems; this is because of the limited value of coupling agent in the nanocomposites. It is well known, through the improvement of the compatibility between neat HDPE and clay (using MA), the polymer chains could be well diffused into the clay layers and the basal spacing of clay layers might be increased.[16–20] In the case of polymers containing polar functional groups, alkyl ammonium surfactant-modified nanoclay is adequate to promote nanocomposite formation. However, in the case of high density polyethylene, it is frequently necessary to use a coupling agent, such as maleic anhydride polyethylene (MAPE).[16–20]

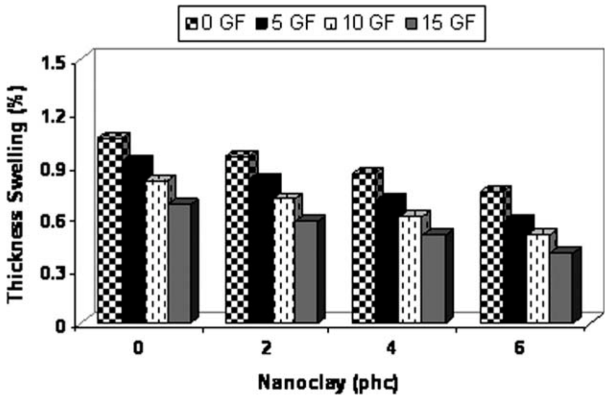

Figure 7 Influence of nanoclay and glass fiber content on thickness swelling of HDPE/RF composites.

TABLE II
Interlayer Spacing and Relative Intercalation in the HDPE/RF Composites

Sample	2θ (Å)	d-spacing (nm)
Pure nanoclay	4.76	18.5
Composite with 2 phc nanoclay	3.70	23.83
Composite with 4 phc nanoclay	3.09	28.47
Composite with 6 phc nanoclay	3.19	27.61

CONCLUSIONS

Hybridization can improve the physical and mechanical properties of natural fiber plastic composites. The results of the present study confirm that it is possible to enhance such properties by adding glass fiber to HDPE/RF plastic composites. Both tensile modulus and strength were improved when glass fibers were added to HDPE/RF composites system but impact strength decreased. Moisture absorption further decreases with the increase of glass fiber content. Also, the result indicated that the tensile modulus and tensile strength of composites increased with increase of nanoclay up to 4 phc and then decreased. However the impact strength and water absorption of the composites decreased with increasing the nanoclay loading. Morphological finding showed that the order of intercalation is higher for 4 phc of nanocaly than 6 phc of nanoclay concentration. Also, the clay dispersion can be improved in the HDPE matrix in the presence of compatibilizer.

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